

Preface

Every hypothesis must derive indubitable results from mechanically well-defined assumptions by mathematically correct methods. If the results agree with a large series of facts, we must be content, even if the true nature of facts is not revealed in every respect. No one hypothesis has hitherto attained this last end, the Theory of Gases not excepted.

Boltzmann, [1, p. 536, #112]

In recent years renewed interest grew about the problems of nonequilibrium statistical mechanics. I think that this has been stimulated by the new research made possible by the availability of simple and efficient computers and of the simulations they make possible.

The possibility and need of performing systematic studies has naturally led to concentrate efforts in understanding the properties of states that are in stationary nonequilibrium: thus establishing a clear separation between properties of evolution towards stationarity (or equilibrium) and properties of the stationary states themselves: a distinction which until the 1970s was rather blurred.

A system is out of equilibrium if the microscopic evolution involves non-conservative forces or interactions with external particles that can be modeled by or identified with dissipative phenomena which forbid indefinite growth of the system energy. The result is that nonzero currents are generated in the system with matter or energy flowing and dissipation being generated. In essentially all problems, the regulating action of the external particles can be reliably modeled by non-Hamiltonian forces.

Just as in equilibrium statistical mechanics the stationary states are identified by the time averages of the observables. As is familiar in measure theory, the collections of averages of any kind (time average, phase space average, counting average, etc.) are in general identified with probability distributions on the space of the possible configurations of a system; thus such probability distributions yield the natural formal setting for the discussions with which we shall be concerned here. Stationary states are identified with probability distributions on the microscopic configurations, i.e. on phase space, which of course have to be invariant under time evolution.

A first problem is that in general there will be a very large number of invariant distributions: which ones correspond to stationary states of a given assembly of atoms and molecules? That is, which ones lead to averages of observables that can be identified with time averages under the time evolution of the system?

This has been a key question already in equilibrium: Clausius, Boltzmann, Maxwell (and others) considered it reasonable to think that the microscopic evolution had the property that, in course of time, every configuration was reached from motions starting from any other.

Analyzing this question has led to many developments since the early 1980s: the purpose of this monograph is to illustrate a point of view about them. My interest on the subject started from my curiosity to understand the chain of achievements that led to the birth of Statistical Mechanics: many original works are in German language; hence I thought it of some interest to present and comment on the English translation of large parts of a few papers by Boltzmann and Clausius that I found inspiring at the beginning of my studies. [Chapter 6](#) contains the translations: I have tried to present them as faithfully as possible, adding a few personal comments inserted in form of footnotes or, if within the text, in slanted characters; original footnotes are marked with “NdA.”

I have not included the celebrated 1872 paper of Boltzmann, [2, #22], on the Boltzmann’s equation, which is widely commented and translated in the literature; I have also included comments on Maxwell’s work of 1866, [3, 4], where he derives and amply uses a form of the Boltzmann’s equation which we would call today a “weak Boltzmann’s equation”: this Maxwell’s work was known to Boltzmann (who quotes it in [5, #5]) and is useful to single out the important contribution of Boltzmann (the “strong” equation for the one particle distribution and the H -theorem).

Together with the many cross references, [Chap. 6](#) makes, hopefully, clear aspects, relevant for the present book, of the interplay between the three founders of modern statistical mechanics, Boltzmann, Clausius, and Maxwell (it is only possible to quote them in alphabetical order) and their influence on the recent developments.

I start, in [Chap. 1](#), with a review of equilibrium statistical mechanics ([Chap. 1](#)) mostly of historical nature. The mechanical interpretation of the second law of thermodynamics (referred here as “the heat theorem”) via the ergodic hypothesis and the least action principle is discussed. Boltzmann’s equation and the irreversibility problem are briefly analyzed. Together with the partial reproduction of the original works in [Chap. 6](#), I hope to have given a rather detailed account of the birth and role (and eventual “irrelevance”) of the ergodic hypothesis from the original “monocyclic” view of Boltzmann, to the “polycyclic” view of Clausius,

to the more physical view of Maxwell¹ and to the modern definition of ergodicity and its roots in the discrete conception of space time.

In Chap. 2 thermostats, whose role is to permit the establishment of stationary nonequilibria, are introduced. Ideally, interactions are conservative and therefore thermostats should ideally be infinite systems that can indefinitely absorb the energy introduced in a system by the action of non-conservative external forces. Therefore, models of infinitely extended thermostats are discussed and some of their properties are illustrated. However, great progress has been achieved since the 1980s by studying systems kept in a stationary state thanks to the action of finite thermostats: such systems have great advantage of being often well suited for simulations. The disadvantage is that the forces driving them are not purely Hamiltonian: however, one is (or should be) always careful that at least they respect the fundamental symmetry of Physics, which is time reversal.

This is certainly very important particularly because typically in nonequilibrium we are interested in irreversible phenomena. For instance, the Hoover's thermostats are time reversible and led to new discoveries (works of Hoover, Evans, Morriss, Cohen, and many more). This opened the way to establishing a link with another development in the theory of chaotic system, particularly with the theory of Sinai, Ruelle, Bowen, and Ruelle's theory of turbulence. It achieved a major result of identifying the probability distribution that in a given context would be singled out among the great variety of stationary distributions that it had become clear would be generically associated with any mildly chaotic dynamical system.

It seems that this fact is not (yet) universally recognized and the SRB distribution is often shrugged away as a mathematical nicety.² I dedicate a large part of Chap. 2 to trying to illustrate the physical meaning of the SRB distribution relating it to what has been called (by Cohen and me) "chaotic hypothesis". It is also an assumption that requires understanding and some open mindedness: personally I have been influenced by the ergodic hypothesis (of which it is an extension to nonequilibrium phenomena) in the original form of Boltzmann, and for this reason I have proposed here rather large portions of the original papers by Boltzmann and Clausius, see Chap. 6. The reader who is perplexed about the chaotic hypothesis can find some relief in reading the mentioned classics and their even more radical treatment of what today would be chaotic motions, via periodic motions. Finally, the role of dissipation (in time reversible systems) is discussed and its remarkable physical meaning of entropy production rate is illustrated (another key discovery

¹ "The only assumption which is necessary for the direct proof is that the system, if left to itself in its actual state of motion, will, sooner or later pass through every phase that is consistent with the equation of energy. Now it is manifest that there are cases in which this does not take place... But if we suppose that the material particles, or some of them, occasionally encounter a fixed obstacle such as the sides of a vessel containing the particles, then, except for special forms of the surface of this obstacle, each encounter will introduce a disturbance into the motion of the system, so that it will pass from one undisturbed path into another...", [6, Vol. 2, p. 714].

² It is possible to find in the literature heroic efforts to avoid dealing with the SRB distributions by essentially attempting to do what is actually done (and better) in the original works.

due to the numerical simulations with finite reversible thermostats mentioned above).

In Chap. 3, theoretical consequences of the chaotic hypothesis are discussed: the leading ideas are drawn again from the classic works of Boltzmann see Sects. 6.2 and 6.12: the SRB distribution properties can conveniently be made visible if the Boltzmann viewpoint of discreteness of phase space is adopted. It leads to a combinatorial interpretation of the SRB distribution, which unifies equilibrium and nonequilibrium relating them through the coarse graining of phase space made possible by the chaotic hypothesis. The key question of whether it is possible to define entropy of a stationary nonequilibrium state is discussed in some detail making use of the coarse grained phase space: concluding that while it may be impossible to define a nonequilibrium entropy it is possible to define the entropy production rate and a function that in equilibrium is the classical entropy while out of equilibrium is “just” a Lyapunov function (one of many) maximal at the SRB distribution.

In Chap. 4 several general theoretical consequences of the chaotic hypothesis are enumerated and illustrated: particular attention is dedicated to the role of the time reversal symmetry and its implications on the universal (i.e., widely model independent) theory of large fluctuations: the fluctuation theorem by Cohen and myself, Onsager reciprocity and Green–Kubo formula, the extension of the Onsager–Machlup theory of patterns fluctuations, and an attempt to study the corresponding problems in a quantum context. Universality is, of course, important because it partly frees us from the nonphysical nature of the finite thermostats.

In Chap. 5 I try to discuss some special concrete applications, just as a modest incentive for further research. Among them, however, there is still a general question that I propose and to which I attempt a solution: it is to give a quantitative criterion for measuring the degree of irreversibility of a process, i.e., to give a measure of the quasistatic nature of a process.

In general, I have avoided technical material preferring heuristic arguments to mathematical proofs: however, when possible references have been given for readers who find some interest in the topics treated and want to master the (important) details. The same applies to the Appendices (A–K).

In Chap. 6 several classic papers are presented, all but one in partial translation from the original German language. These papers illustrate my personal route to studying the birth of ergodic theory and its relevance for statistical mechanics, [7–11] and, implicitly, provide motivation for the choices (admittedly very personal) made in the first five chapters and in the Appendices.

Appendices A–K contain a few complements, and the remaining appendices deal with technical problems that are still unsolved. Appendix M (with more details in appendices N, O, P) gives an example of the work that may be necessary in actual constructions of stationary states in the apparently simple case of a forced pendulum in presence of noise. Appendices Q–T discuss an attempt (*work in progress*) at studying a stationary case of BBGKY hierarchy with no random forces but out of equilibrium. I present this case because I think it is instructive

although the results are deeply unsatisfactory: it is part unpublished work in strict collaboration with G. Gentile and A. Giuliani.

The booklet represents a viewpoint, my personal, and does not pretend to be exhaustive: many important topics have been left out (like [12–15], just to mention a few works that have led to further exciting developments). I have tried to present a consistent theory including some of its unsatisfactory aspects.

The Collected papers of Boltzmann, Clausius, Maxwell are freely available: about Boltzmann I am grateful (and all of us are) to Wolfgang Reiter, in Vienna, for actively working to obtain that *Österreichische Zentralbibliothek für Physik* undertook and accomplished the task of digitizing the “Wissenschaftliche Abhandlungen” and the “Populäre Schriften” at

https://phaidra.univie.ac.at/detail_object/o:63668

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respectively, making them freely available.

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Giovanni Gallavotti

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